

HYDROXYLAPATITE CERAMIC

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of copending application Ser. No. 707,315, filed Jul. 21, 1976, now abandoned which is a continuation-in-part of application Ser. No. 593,303, filed Jul. 7, 1975, now abandoned and which is in turn a continuation-in-part of application Ser. No. 494,240, filed Aug. 2, 1974, now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The subject matter of this invention resides in the field of ceramics and finds particular utility in the areas of dentistry, orthopedics, electronics and electrical engineering.

2. Description of the Prior Art

Much current dental research is focused on the preparation of materials which can be used as a substitute for tooth and bone, as a dental restorative material for fillings, caps and crowns and as a prosthetic filling material for bone. Dental research also is directed to preventing the formation of dental plaque, the putative agent of both dental caries and periodontal disease.

Currently used filler materials for dental restorative compositions such as quartz, alumina, silicates, glass beads, etc., bear little chemical or physical resemblance to tooth enamel. A particular deficiency of these materials lies in the incompatibility of the linear coefficients of expansion of filler material and tooth which can eventually result in marginal leakage and new caries formation. The dental profession, therefore, has long desired a dental filling composition with physical properties which closely conform to those of natural tooth structure.

Furthermore, in the field of surgical prosthetic materials, which is currently dominated by high-strength, non-corrosive alloys, there is a recognized need for a material which more closely resembles biological hard tissue as the problems of tissue acceptance and adherence have not as yet been completely resolved [Hulbert, et al., *Materials Science Research* 5, 417 (1971)].

In research directed to the discovery of effective anti-plaque chemotherapeutic agents there is need for a standard test material having a tooth-like surface with respect to both plaque formation and substantiveness of chemical agents. Although natural teeth have been used for this purpose, these have the drawbacks of being highly variable, relatively unavailable in large numbers, and require elaborate cleaning before use. Consequently there are used other materials upon which dental plaque will accumulate such as powdered hydroxylapatite, acrylic teeth, glass and wire. Although perhaps adequate for studying plaque formation as such, these materials bear little resemblance to the natural tooth surface and are therefore not completely suitable for use in finding effective anti-plaque agents. For example, it is known that chemicals which inhibit plaque formation on teeth do not necessarily do so on glass and wire [Turesky et al., *J. Periodontology* 43, 263 (1972)]. There is a need then for an inexpensive, readily available material which is chemically similar to tooth enamel, hard, dense, and highly polished.

Hydroxylapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, also known as basic calcium orthophosphate, occurs as a mineral in

phosphate rock. It constitutes the mineral phase of tooth and bone and has been suggested as suited to the various purposes outlined above.

U.S. Pat. No. 2,508,816, issued May 23, 1950 discloses a method for obtaining the hydroxylapatite of tooth enamel and its use in admixture with a synthetic resin as a prosthetic tooth composition. This procedure is lengthy and laborious and limited to producing finely divided hydroxylapatite. Moreover, the method is of course dependent on the availability of a supply of natural teeth.

The use of porous, non-ceramic hydroxylapatite as a filler material in dental cements and filling compositions has been disclosed, e.g. in U.S. Pat. No. 3,873,327, issued Mar. 25, 1975 on an application filed Feb. 28, 1974 and German Offenlegungsschrift 2,415,333 published Oct. 17, 1974.

Kutty [Indian J. Chem. 11, 695 (1973)] has reported the results of a study of the thermal decomposition of hydroxylapatite which indicate in summary that "Hydroxylapatite, $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$, undergoes a slow decomposition when heated at 1250° C. in a current of dry air, forming a mixture of $\text{Ca}_3(\text{PO}_4)_2$ and $\text{Ca}_4\text{P}_2\text{O}_9$ as confirmed by IR and X-ray diffraction studies."

The report also described the heating of powdered synthetic hydroxylapatite at 1050° C. and 1150° C. for 20 hours. Excepting the statement that the sample heated at 1150° C. underwent partial decomposition as indicated by infrared and X-ray diffraction data, the report neither described nor characterized the products obtained by heating below 1250° C. nor are said products stated or suggested to have any utility.

Bett, et al. [*J. Amer. Chem. Soc.* 89, 5535 (1967)] described the preparation of particulate hydroxylapatite with stoichiometry varying from Ca/P = 1.67 to 1.57. The materials so-produced contained large intercrystalline pores. It was also reported that upon heating up to 1000° C. the calcium-deficient hydroxylapatites underwent partial transformation to the whitlockite phase.

McGee (U.S. Pat. No. 3,787,900, filed June 9, 1971, issued Jan. 29, 1974) disclosed a bone and tooth prosthetic material comprising a refractory compound and a calcium phosphate compound, e.g. whitlockite.

Several attempts have been made to provide a hard, strong macroform of hydroxylapatite. However, none of the previously known forms of hydroxylapatite has proven fully satisfactory. Thus, Della M. Roy and S. K. Linnehan [*Nature*, 247, 220 (1974); U.S. Pat. No. 3,929,971, filed Mar. 30, 1973, issued Dec. 30, 1975] described an elaborate hydrothermal exchange process whereby the skeletal calcium carbonate of marine coral was converted to hydroxylapatite. The material so produced necessarily retained the high porosity characteristic of the coral structure and moreover had a relatively low tensile strength of about 270-470 psi, a serious disadvantage in a prosthetic material.

Monroe, et al. [*Journal of Dental Research* 50, 860 (1971)] reported the preparation of a ceramic material by sintering compressed tablets of synthetic hydroxylapatite. The material so produced was actually a mixture of hydroxylapatite and approximately 30 percent α -whitlockite, which is $\text{Ca}_3(\text{PO}_4)_2$ or tricalcium phosphate, as an ordered mosaic array of polyhedral crystallites, and appeared too porous to make it suitable for use in a dental material.

Rao and Boehm [*Journal of Dental Research* 53, 1351 (1974)] disclosed a polycrystalline form of hydroxylapatite prepared by isostatically pressing powdered hy-